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Sublimation via virtual melting inside an elastoplastic material

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Thermodynamic, kinetic, and mechanical approaches for sublimation inside elastoplastic material via intermediate (virtual) melting under tensile pressure are developed for a spherical nucleus. Virtual melting represents the appearance of subcritical liquid drop that immediately transforms to gas bubble. The variety of mechanisms and transformation paths are revealed in different pressure ranges. The radius of the critical gas nucleus differs from the classical one because elastic energy of melt is size dependent due to surface tension. Our developed approach can be extended for various structural changes in nanoparticles within a void inside elastoplastic material and two-stage and multistage nucleation processes. Universal mechanical gas bubble instability is revealed.

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Recently,¹ we developed thermodynamic and kinetic approaches to sublimation within elastoplastic material under applied tensile pressure, which are important, for example, for sublimation in unloading waves during laser ablation or in core-shell nanoparticles after dynamic shell fracture.² Several conceptual problems were resolved and unexpected scenarios were revealed. Pressure significantly grows within a bubble due to the large volume increase, leading to large plastic deformations around the bubble. It requires an application of large-strain continuum mechanic formulations. Plastic dissipation makes classical thermodynamic approaches, based on the change in Gibbs energy as the driving force for sublimation, nonapplicable. Thus, several possible nucleation paths were worked out, expressions for corresponding driving forces and activation energies were derived, and the kinetic relations between sublimation temperature and pressure were calculated. Related phenomena include expansion of a subcritical gas nucleus into a supercritical one due to mechanical instability (rather than due to solid-gas transformation) or its shrinking into a stable void, as well as path dependence of activation energy.

In this Brief Report, an alternative mechanism of gaseous bubble nucleation, namely, via intermediate (virtual) melting, is suggested and studied using an extension of the thermodynamic and the kinetic approaches developed in Ref. 1. Our results, presented in Fig. 1, exhibit a variety of mechanisms and transformation paths leading to appearance of a gas bubble in different pressure ranges. Above tensile pressure p_5 , direct sublimation occurs at the lowest temperature θ_s^d , while below p_5 the thermodynamic equilibrium melting temperature θ_m^q becomes smaller than the kinetic sublimation temperature. While it is not sufficient for nucleation of supercritical liquid nucleus, plenty of subcritical liquid drops exist inside solid in the pressure range $p_3 < \sigma < p_5$. As soon as the kinetic criterion for vaporization of some of them is met at temperature θ_s^m , subcritical liquid droplets immediately transform into critical gas bubbles below the kinetic sublimation θ_s^d and melting θ_m , temperatures. Thus, in the pressure range $p_3 < \sigma < p_5$, melt represents an intermediate transitional state between solid and gas; as soon as subcritical

cal melt nucleus appears, it immediately becomes unstable with respect to gas. That is why we called this melt “virtual melt,” similar to the virtual melt along the path between two crystalline phases or between crystal and amorphous phases,^{3,4} which we predicted earlier.

Main assumptions, their justifications, and the limitations of our approach are similar to those in Ref. 1. We will use s , m , and g for solid, melt, and gas phases, respectively. For sublimation via virtual melting, we will consider two subsequent processes: first, a solid sphere of radius r_s homogeneously transforms into liquid drop of the radius r_m within an infinite elastoplastic sphere and, second, a homogeneous transformation of the *entire* liquid drop into a gas bubble of the radius r_g occurs within an elastoplastic sphere. Plastic deformation and dissipation occur in a solid in a hollow spherical region around transforming particle. The thermodynamics of melting in an elastoplastic sphere was developed in Refs. 5 and 6; here, we will add surface effects and kinetics. Some points of the thermodynamic and the kinetic descriptions of the transformation of virtual melt into gas inside an elastoplastic sphere are similar to that which we developed for sublimation in Ref. 1 but there are some essential differences. The second process is a transformation in nanosize particles. The main distinction is that the melt drop experiences size-dependent surface tension, which contributes to the energy of the elastic stresses. Thus, maximization of activation energy with respect to the particle size leads to an expression different from the classical one and from that obtained in “nanothermodynamics.”⁷ This is one more difference from classical nucleation theory, in addition to alternative expression for the driving force (due to plastic dissipation) and the allowance for large strains.

The driving force X for the homogeneous transformations s - m and m - g coincides with the total dissipation that can be determined based on the second law of thermodynamics:⁶ $X^{sm} = X_v^{sm} V_s - \Gamma_{sm} S^{sm}$, $X^{mg} = X_v^{mg} V_s - (\Gamma_{sg} S^{sg} - \Gamma_{sm} S^{sm})$, where V_s is the volume of transformed solid, $S = 4\pi r^2$ is the surface of the nucleus, Γ is the interface energy, and

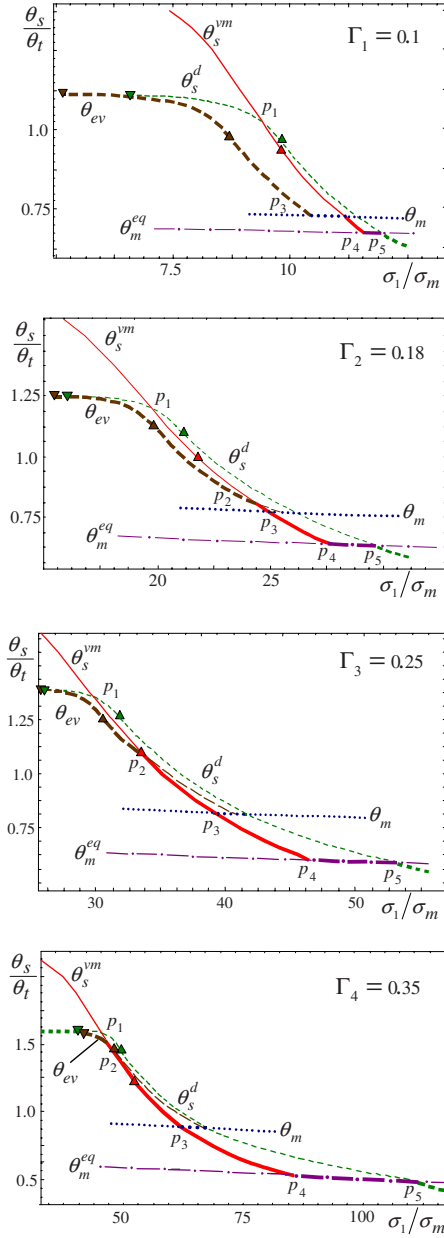


FIG. 1. (Color online) Calculated temperature-tensile pressure curves for the appearance of a spherical liquid drop and gas bubble within elastoplastic solid and liquid for four values of solid-gas surface energy (shown in the right corner in J/m^2). The curves are for sublimation temperature via virtual melting θ_s^{vm} (red solid line), for melting θ_m (blue dotted line), for direct sublimation θ_s^d (green dashed line), for evaporation of melt θ_{ev} (brown long-dashed-style line), and for thermodynamic equilibrium melting curve θ_m^{eq} (magenta long-dashed-dotted-style line). Bold parts of curves correspond to the lowest temperature for a given tensile pressure at which critical gas nucleus can appear. They correspond to direct sublimation above p_5 , sublimation via virtual melting $p_2 < \sigma < p_5$, and evaporation of liquid below p_2 . Melting can occur below p_3 , and it competes with gas formation. For temperatures below the values marked with \blacktriangledown , gas nucleus cannot grow due to solid-gas transformation, but it loses its mechanical stability and expands like a balloon, reaching critical size for solid-gas transformation. For temperatures below the values marked with \blacktriangle , the critical radius of transformed solid reaches its minimum value $r_c^s = r_{s,\text{min}}$.

$$X_v = -W - \rho_s \Delta\psi \quad (1)$$

is the volumetric driving force for transformation per unit volume of solid, with W representing mechanical work, ρ being the mass density, and $\Delta\psi$ being the change in the Helmholtz free energy per unit mass. For melting, the radial stress σ_r in solid at the m - s interface and its mechanical work are^{5,6}

$$\sigma_r^m = -\sigma + \frac{2}{3}\sigma_y \left(1 + \ln \frac{K\epsilon_0}{\sigma_y C}\right), \quad (2)$$

$$W_m = -\sigma\epsilon_0 + \frac{2}{3}\sigma_y\epsilon_0 \left(\frac{\sigma_y C}{2K\epsilon_0} + \ln \frac{K\epsilon_0}{\sigma_y C}\right), \quad (3)$$

where σ_y is the yield strength, $C = (1-\nu)/(1-2\nu)$, ν is the Poisson's ratio, K is the bulk modulus, and ϵ_0 is the volumetric transformation strain during melting. The von Mises plasticity condition, $\sigma_\phi - \sigma_r = \sigma_y$, was used, where σ_r and σ_ϕ are the radial and the circumferential stresses in a solid at the m - s interface. Because normally $\epsilon_0 < 0.1$, small-strain theory was used with elastic strains being included. For the m - g transformation, we utilized our modification¹ of the solution to the large-strain problem in Ref. 8,

$$\sigma_r^g = -\sigma + \frac{2}{3}\sigma_y \left\{1 + \ln \left[\frac{K}{\sigma_y C} \left(1 - \frac{1}{a}\right) \right] \right\}, \quad (4)$$

where $a = V/V_s$ and $V = 4/3\pi r^3$ is the volume of the transforming sphere after transformations. To obtain an analytical solution, elastic strains are neglected. Then,

$$W_g = \int_{a_0}^{a_g} \sigma_r da = -(a - a_0)\sigma + \frac{2}{3}\sigma_y \left[(a - a_0) + \ln \left(\frac{\epsilon_0}{\epsilon} \right) + a \ln \left(\frac{\epsilon K}{a C \sigma_y} \right) - a_0 \ln \left(\frac{\epsilon_0 K}{a_0 C \sigma_y} \right) \right], \quad (5)$$

where $a_0 = 1 + \epsilon_0$ corresponds to melt drop with neglected elastic strain and $\epsilon = a - 1$. From the mechanical equilibrium at the m - s and the s - g interfaces,

$$p_m = \sigma_r^m + 2\Gamma_{ms}/r_m, \quad p_g = \sigma_r^g + 2\Gamma_{gs}/r_g, \quad (6)$$

where p_m and p_g are the pressures in melt and gas, respectively. Note that we used σ_r in solid rather than p_m or p_g in mechanical work evaluation because it represents the work of external stresses for the nucleus. Since we included change in interface energy, the external surface should be infinitesimally outside the interface—i.e., in solid. We consider an ideal gas and the simplest quadratic elastic energy of melt and solid,

$$p_g = \rho R \theta / M a, \quad \psi_g = \psi_g^\theta - \frac{R\theta}{M} \ln \left(\frac{p_0}{p_g} \right),$$

$$\psi_s = \psi_s^\theta + \frac{\sigma^2}{2K\rho_s}, \quad \psi_m = \psi_m^\theta + \frac{p_m^2}{2K\rho_m}, \quad (7)$$

where θ_0 and p_0 are the reference temperature and pressure, M is the molecular mass, R is the gas constant, and ψ^θ is the thermal part of free energy per unit mass. We as-

sume that for both the s - m and the m - g transformations, $\Delta\psi^\theta = \Delta\psi_0^\theta - \Delta s(\theta - \theta_0)$, where the constants $\Delta\psi_0^\theta$ and Δs are the jumps in reference free energy and entropy. An activation energy is defined as $Q = -\min X$ with respect to V_s . Then the critical volume of the solid V_c^m that transforms to melt and corresponds to $\min X$ and the corresponding activation energy are

$$V_c^m = (32\pi a_m^2 \Gamma_{sm}^3) / (3X_{v,sm}^3),$$

$$Q_{sm} = 16\pi a_m^2 \Gamma_{sm}^3 / (3X_{v,sm}^2) = 80k\theta, \quad (8)$$

where k is the Boltzmann constant. The kinetic phase transformation criterion $Q = 80k\theta$ [more generally $Q = (40-80)k\theta$] is determined from the condition that, for larger Q , nucleation time exceeds any realistic time of observation; this criterion is widely used in the literature (e.g., see Refs. 1 and 9 and references therein). For the m - g transformation, the expression for the critical nucleus is different because the elastic energy of melt through p_m and Eq. (6) depends on a radius of nucleus. Because the entire melt drop transforms into a gas bubble, the radius of melt drop is also varied. Using $r_g = r_s a_g^{1/3}$ and $r_m = r_s a_m^{1/3}$ and minimizing

$$X^{mg} = 4/3\pi r_s^3 \{A + \rho_s[\sigma_r^m + 2\Gamma_{sm}/(r_s a_m^{1/3})]^2 / (2K)\} - 4\pi r_s^2 (\Gamma_{sg} a_g^{2/3} - \Gamma_{sm} a_m^{2/3}) \quad (9)$$

with respect to r_s , where $A = -W - \rho_s \psi_g + \rho_s \psi_m^\theta$, we obtain the critical radius of the solid that transforms to gas via virtual melt,

$$r_g^c = [-x_2 - \text{sign}(x_2) \sqrt{x_2^2 - 16x_1 \rho_s \Gamma_{sm}^2}] / x_1 \quad (10)$$

with $x_1 = 3a_m^{2/3}(2AK + \rho_s \sigma_r^m)$ and $x_2 = 4a_m^{1/3}(2\rho_s \Gamma_{sm} \sigma_r^m + 3a_m \Gamma_{sm} K - 3a_g^{1/3} a_m^{1/3} \Gamma_{sg} K)$. The term $-\text{sign}(x_2)$ in front of the square root is chosen because for $\Gamma_{sm} = 0$ radius r_g^c should not be zero for any $\text{sign}(x_2)$. Substituting r_g^c in the expression for

$$Q^{mg} = -X^{mg}(r_g^c) = 80k\theta, \quad (11)$$

we obtain the kinetic nucleation relations between the temperature for sublimation via virtual melting θ_s^{vm} and tensile pressure σ . Thus, the complete system includes Eqs. (1), (4)–(7), and (9)–(11) for sublimation via virtual melting and Eqs. (1)–(3) and (6)–(8) for melting.

To find the θ_s^{vm} - σ relation for sublimation via virtual melting, we first assume the existence of a melt nucleus that completely transforms to gas. Neglecting elastic deformation of melt, we obtain $a_m = a_0 = \text{const}$. Then r_g^c in Eq. (10) (as well as all parameters in melt and gas and activation energy) can be expressed in terms of σ , θ , and a_g . For a prescribed θ_s^{vm} and a number of values of σ , substituting the radius of the solid nucleus transformed in melt and then in gas r_g^c [Eq. (10)] into the second equilibrium Eq. (6), we can find the relationship $a_g(\sigma)$. Substituting it into Eq. (11) for Q^{mg} , the stress σ can be found, and then the critical radius r_g^c can be found from Eq. (10). We check whether $r_g^c > a_g^{1/3} r_{s,min}$, where $r_{s,min}$ is the minimal radius of the transformed solid for which V contains enough molecules to talk about gas. Otherwise, we use $r_g^c = a_g^{1/3} r_{s,min}$ and repeat the same procedure. After the

critical nucleus is found, we check its mechanical stability $p_g(a) < \sigma_r^g + \frac{2\Gamma_{mg}}{r_s a_g^{1/3}}$ for the prescribed r_s^c —i.e., for the mechanical expansion of a gas without solid-gas transformation. In the same way, we find equation $\theta_m(\sigma)$ for the appearance of critical melt nucleus in solid. Calculations were performed for the following data (which are close to the data for energetic crystal HMX, if known): $\theta_0 = 298.15$ K, $p_0 = 1$ bar, $\Delta s = 1.031$ J/K kg, $\Delta\psi_0^\theta = 379.515$ J/g, reference mass density of gas $\rho_{0g} = 10.1 \times 10^{-3}$ g/cm³ and solid $\rho_s = 1.71$ g/cm³, $M = 250.151$ kg/mol, $K = 15$ GPa, $\sigma_y = 2.6$ MPa, $\epsilon_0 = 0.067$, $\Gamma_{sm} = 1/3 \Gamma_{sg}$, and $r_{min} = 0.3$ nm.

The results are presented in Fig. 1 for different surface energies. Sublimation temperature and pressure are divided by $\theta_t = 784.12$ K (defined from $X_v = 0$ at $\sigma_1 = 0$) and $\sigma_m = 15.77$ MPa [pressure for unlimited plastic expansion of the cavity for $\Gamma = 0$ (Ref. 1)], respectively. The curve for sublimation temperature via virtual melting $\theta_s^{vm}(\sigma)$ passes through points $p_1 p_2 p_3 p_4$. We did not continue the $\theta_s^{vm}(\sigma)$ curve below the thermodynamic melting line $\theta_m^e(\sigma)$ $p_4 p_5$, which was determined from the condition $X_v^{sm} = 0$. For temperatures below the point marked with \blacktriangledown on the curve $\theta_s^{vm}(\sigma)$, the gas nucleus loses its mechanical stability and expands. That means that, although the growth of this nucleus due to solid-gas transformation is impossible (i.e., it is subcritical from the classical point of view, similar to the case of direct sublimation¹), it will expand like a balloon up to the critical size when growth due to phase transition is possible. We found that this mechanical instability occurs not only in elastoplastic solid but also in the classical theory of gas nucleation in liquid (below the point marked with \blacktriangledown on the curve θ_{ev}). Thus, this is a universal mechanical instability of a gas bubble, which was overlooked in classical nucleation theory. For temperatures below the point marked with \blacktriangle on the curve $\theta_s^{vm}(\sigma)$, the critical radius for gas nucleus $r_g^c = a_g^{1/3} r_{s,min}$.

Each figure also contains the direct sublimation line $\theta_s^d(\sigma)$ $p_1 p_5$, taken from Ref. 1 and the calculated melting line $\theta_m(\sigma)$. Thus, pressures p_1 , p_3 , p_4 , and p_5 correspond to the intersection of the curves for direct sublimation and sublimation via virtual melting, for sublimation via virtual melting and melting, for sublimation via virtual melting and the equilibrium melting curve, and for direct sublimation and equilibrium melting, respectively. Along the line $p_3 p_4 p_5$ ($p_3 < \sigma < p_5$), critical melt nucleus cannot appear because it is below the $\theta_m(\sigma)$ curve. However, for the determined radius of the virtual melt nucleus that further transforms to gas along the line $p_3 p_4 p_5$, $r^m = a_m^{1/3} r_{s,min}$, the activation energy for virtual melting is smaller than $80k\theta$. Thus, while such melt nuclei are subcritical and cannot grow, the probability of their appearance is high because of the small activation energy, and they may transform to gas because the kinetic criterion for gas nucleation is fulfilled for them along the line $p_3 p_4 p_5$.

For $\sigma < p_3$ along the line θ_m , critical melt nucleus appears, and its growth may lead to complete melting. Then, using classical homogeneous nucleation theory, we can determine the kinetic curve $\theta_{ev}(\sigma)$ for the appearance of critical gas nucleus in liquid—i.e., for evaporation. This curve is below the direct sublimation curve and intersects the curve for sub-

limation via virtual melting at pressure p_2 . The higher-pressure process can occur, if the characteristic time of pressure growth is significantly shorter than the characteristic time of the lower-pressure process, if the corresponding kinetic criterion is satisfied, and if the higher-pressure process is faster than the lower-pressure process.

To summarize, the nontraditional sublimation mechanism inside elastoplastic material under tensile stress via virtual melting is justified both thermodynamically and kinetically. It consists of the appearance of subcritical liquid drop, which transforms into a critical gas bubble in some range of tensile pressures and temperatures. While this gas bubble cannot grow due to solid-gas phase transformation, it expands first as a balloon to the critical size due to mechanical instability, and then solid-gas transformation contributes as well. This mechanical instability of a gas bubble is universal—i.e., it occurs within elastoplastic solid and liquid (that is, in the classical theory of gas nucleation in liquid). The richness of the mechanisms and phenomena that lead to gas bubble formation under nontraditional conditions is demonstrated. The method to check our predictions is similar to that described in Ref. 1. As the next step, void nucleation (both direct and via virtual melting) will be studied, and its competition with sublimation will be analyzed.

The idea and problem formulation of two-stage gas nucleation, a complete system of mechanical, thermodynamic, and kinetic equations for two-stage nucleation, as well as the analysis of results in terms of the kinetic tensile pressure-temperature diagram give an idea to researchers from various fields about how to suggest and check two-stage (and multistage) nucleation scenarios for various structural

changes. For example, the following scenarios can be considered: void nucleation/solid-solid transformation (or melting), the same with crack instead of void, virtual melting/void (crack) nucleation, virtual melting/cavitation, solid-solid transformation/crack (void) nucleation, solid-solid transformation/sublimation, solid-solid transformation/dislocation nucleation, and so on.

The second process, namely, transformation of liquid drop into gas bubble represents a typical example of phase transformation in nanoscale systems (nanothermodynamics), which is now under intense study. In the literature, there are many problems with defining correct transformation conditions even without elastoplastic surroundings (see, e.g., Ref. 7). We developed in this Brief Report the framework and equations for a strict treatment of phase transformation in nanoscale systems within elastoplastic materials, when the classical definition of the driving force and activation energy is not applicable and strains are large. Processes that can be studied include phase transformations (solid-solid, solid-melt, and solid-gas) in particles within nanovoids or in nanoparticles covered by shells (e.g., aluminum particles inside of alumina shells²) and cavitation (void nucleation) within nanoparticles embedded in elastoplastic surroundings. One more important result for nanoscale systems is that allowance of surface tension leads to size-dependent pressure and elastic energy, as well as to a much more sophisticated expression for the radius of the critical nucleus than the one in the classical nucleation theory.

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